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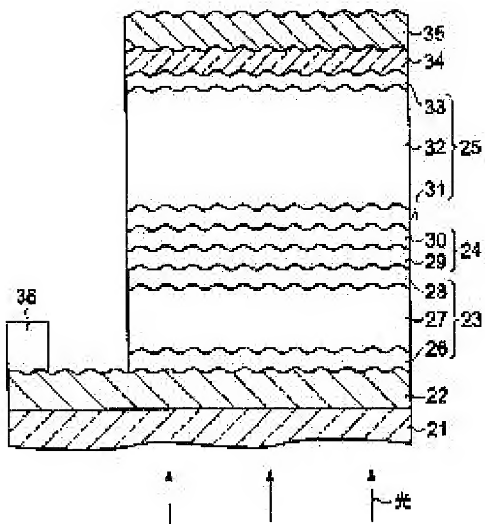
(54) **TANDEM TYPE SILICON-BASED THIN-FILM PHOTOELECTRIC CONVERSION DEVICE**



(57)Abstract:
PROBLEM TO BE SOLVED: To provide a tandem type silicon-based thin-film photoelectric conversion device excellent in stability with advantages that can avoid the generation of a defective part in a unit interface joining part, that can confine each wavelength band having predetermined sensitivity in each unit, and that has a high photoelectric conversion characteristic.
SOLUTION: The tandem type silicon-based thin-film photoelectric conversion device is comprised of a plurality of photoelectric conversion units 23, 25 stacked as two stages on a substrate 21. The photoelectric conversion units 23, 25 has first conductive semiconductor layer 26, 31, silicon-based thin-film photoelectric conversion layers 27, 32 and second conductive semiconductor layer 28, 33, respectively. A composite oxide layer of indium oxide and tin oxide or two layers comprised of a tin oxide layer and a zinc oxide layer are interposed as an intermediate layer 24 between the photoelectric conversion units 23, 25.

[Claim(s)]
[Claim 1]the [which was laminated one by one on a substrate] -- the [1 and] -- it being a tandem-die silicon system thin film photoelectric conversion device which has a photoelectric conversion unit of two, and said each photoelectric conversion unit, A tandem-die silicon system thin film photoelectric conversion device having a semiconductor layer of the 1st conductivity type laminated one by one, a photoelectric conversion layer of a silicon system thin film, and a semiconductor layer of the 2nd conductivity type, respectively, and making an interlayer intervene between said each photoelectric conversion unit.
[Claim 2]The tandem-die silicon system thin film photoelectric conversion device according to claim 1, wherein said interlayer consists of two-layer [of indium oxide and a tin oxide composite oxide layer or a tin oxide layer located in said substrate side, and a zinc oxide layer formed on this].
[Claim 3]The tandem-die silicon system thin film photoelectric conversion device according to claim 2, wherein thickness of indium oxide and a tin oxide composite oxide layer which constitutes said interlayer or a tin oxide layer, and a zinc oxide layer is 5-100 nm, respectively.

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the

tandem-die silicon system thin film photoelectric conversion device containing two or more photoelectric conversion units laminated by two steps on the substrate.

[0002]

[Description of the Prior Art] Development of the photoelectric conversion device using the thin film containing crystalline substance silicon like recent years, for example, polycrystalline silicon, and microcrystal silicon is performed energetically. Such development is a trial in which low-cost-izing and highly-efficient-izing of a photoelectric conversion device will be reconciled, by forming a good silicon thin film by a low temperature process on a cheap substrate. The application to various photoelectric conversion devices, such as a photosensor, is expected from the solar cell.

[0003] Especially, the method of forming the crystalline silicon system thin film photoelectric conversion device which has the photoelectric conversion efficiency outstanding only according to the low temperature process 400 ** or less which can use cheap low melting glass is in the limelight recently. For example, the photoelectric conversion device including the pin junction of microcrystal silicon is indicated to Appl.Phys, Lett., vol.65, and p.860. This photoelectric conversion device is characterized by all these semiconductor layers being microcrystal silicon including the p type semiconductor layer, i-type semiconductor layer, and n type semiconductor layer which were laminated one by one with plasma CVD method simple.

[0004] In the crystalline silicon system thin film photoelectric conversion device by which low-temperature formation is similarly carried out with plasma CVD method, The silicon system thin film which has the upper surface of the texture structure which includes detailed unevenness even if a substrate and a foundation layer are flat surfaces substantially can be formed, It is known that what is called an optical confinement effect that the light which entered into the silicon system thin film becomes difficult to escape outside according to the texture

structure will be acquired.
[0005]In the tandem-die photoelectric conversion device which made an amorphous silicon system thin film photoelectric unit and two steps of crystalline substance system photoelectric conversion units laminate, many reports said that a synthetic photoelectric transfer characteristic improves are made (JP,10-294481,A etc.).
[0006]The tandem-die photoelectric conversion device of JP,10-294481,A has composition shown in drawing 4. The code number 1 in a figure is a substrate, and the photoelectric conversion units 3 and 4 are laminated by two steps via the rear electrode 2 on this substrate 1. One photoelectric conversion unit 3 comprises the one conductivity type layer 5 laminated one by one by the plasma process, the photoelectric conversion layer 6 of the silicon system thin film containing a crystalline substance, and the reverse conductivity type semiconductor layer 7. The photoelectric conversion unit 4 of another side comprises the one conductivity type layer 8 laminated one by one by the plasma process, the photoelectric conversion layer 9 of the silicon system thin film containing a crystalline substance, and the reverse conductivity type semiconductor layer 10. On said photoelectric conversion unit 4, the front transparent electrode 11 and the comb shaped electrode 12 are formed one by one.
[0007]Also in any of a report of drawing 4 and other examples, it is the feature of carrying out assignment absorption of the light of a large wavelength area in several of those different photoelectric conversion units, by combining with a different light wavelength region two or more photoelectric conversion units which have sensitivity.
[0008]
[Problem(s) to be Solved by the Invention]However, according to the conventional technology of drawing 4, it has a problem described below.
1) On a membrane formation process, in laminating two sorts of photoelectric conversion units, the counter diffusion of an

element happens by a unit interface, a defective part occurs in an interface joined part, and original performance cannot be obtained.

[0009]2) In order to make the light of a large wavelength area share and absorb in several of those different photoelectric conversion units, are made by combining with a different light wavelength region two or more photoelectric conversion units which have sensitivity, but. In order to carry out more efficiently, it is necessary to confine in the unit each light wavelength region which has sensitivity.

[0010]this invention is what was made in consideration of the above-mentioned situation -- the -- the [1 and], while being able to prevent a defective part from occurring at the unit community interview rear by making an interlayer intervene between the photoelectric conversion units of two, It aims at providing the highly efficient tandem-die silicon system thin film photoelectric conversion device which can confine in each unit each wavelength band which has predetermined sensitivity, has it, and has a high photoelectric transfer characteristic, and is excellent also in stability.

[0011]

[Means for Solving the Problem]the [by which this invention was laminated one by one on a substrate] -- the [1 and] -- it being a tandem-die silicon system thin film photoelectric conversion device which has a photoelectric conversion unit of two, and said each photoelectric conversion unit, It is a tandem-die silicon system thin film photoelectric conversion device having a semiconductor layer of the 1st conductivity type laminated one by one, a photoelectric conversion layer of a silicon system thin film, and a semiconductor layer of the 2nd conductivity type, respectively, and making an interlayer intervene between said each photoelectric conversion unit.

[0012]In this invention, what consists of two-layer [of indium oxide and a tin oxide composite oxide layer (ITO layer) or a tin oxide layer located in said substrate side, for example, and a zinc oxide layer formed on this] as said interlayer is

mentioned. Here, an ITO layer or a tin oxide layer was chosen as the substrate side because conductivity formed at low temperature highly. Since a zinc oxide uses hydrogen so much when it forms a semiconductor layer which is strong to plasma resistance and constitutes the 2nd photoelectric conversion unit by plasma CVD, forming a zinc oxide layer on it, It is for avoiding that indium oxide and a tin oxide composite oxide layer (ITO layer), or a tin oxide layer located in the substrate side is returned.

[0013]As for thickness of indium oxide and a tin oxide composite oxide layer which constitutes said interlayer or a tin oxide layer, and a zinc oxide layer, it is preferred that it is 5-100 nm, respectively. This is because incident light intensity of long wavelength light sent to the 2nd photoelectric conversion unit among incident light by the side of a substrate will decrease substantially if an impurity cannot be prevented from being mixed in a unit of another side but thickness exceeds 100 nm, when thickness is less than 5 nm.

[0014]according to this invention -- the -- the [1 and] -- by making an interlayer having a counter diffusion preventing function between units, a current compensation function, and a predetermined optical function intervene between photoelectric conversion units of two, While being able to prevent a defective part from occurring at the unit community interview rear, a highly efficient tandem-die silicon system thin film photoelectric conversion device which can confine in each unit each wavelength band which has predetermined sensitivity, has it, and has a high photoelectric transfer characteristic, and is excellent also in stability can be obtained. By laminating a crystalline silicon system thin film photoelectric conversion module, It is possible for reliability and stability of a photoelectric conversion device to be improved remarkably, and to also attain highly efficient-ization of a photoelectric conversion device accompanying improvement in the optical confinement effect, and it can contribute to utilization of a silicon system thin film

photoelectric conversion device greatly.

[0015]

[Embodiment of the Invention]Drawing 1 shows the typical sectional view of the two-step tandem-die silicon system thin film photoelectric conversion device concerning an example of the embodiment of this invention. The code number 21 in a figure shows a substrate. Here, as the substrate 21, a cheap glass substrate is used, for example with an organic film or a low melting point. On said substrate 21, the surface electrode 22 which consists of tin oxide (SnO_2) is formed by vacuum deposition, the sputtering technique, or the heat CVD method.

[0016]On said rear electrode 22, the 1st step of 1st photoelectric conversion unit 23, the interlayer 24, and the 2nd step of 2nd photoelectric conversion unit 25 are formed one by one. Here, the 1st photoelectric conversion unit 23 has the high sensitivity of short wavelength (300-800 nm), and the 2nd photoelectric conversion unit 25 has the high sensitivity of long wavelength (500-1200 nm). Said photoelectric conversion unit 23 comprises the semiconductor layer 26 of the 1st conductivity type, the photoelectric conversion layer 27, and the semiconductor layer 28 of the 2nd conductivity type.

[0017]Said semiconductor layer 26 is deposited with plasma CVD method, and either the microcrystal silicon thin film in which the conductivity-type impurity atom was doped, or an amorphous silicon thin film is used. In the case of a p type layer, as an impurity atom, boron atoms are used for the semiconductor layer 26, for example. The thickness of a semiconductor layer is set up within the limits of 3-100 nm, and is more preferably set up within the limits of 5-50 nm.

[0018]Said photoelectric conversion layer 27 is obtained by forming a microcrystal silicon thin film or an amorphous silicon thin film with plasma CVD method. As said photoelectric conversion layer 27, non-doped i type amorphous silicon thin film and i type microcrystal silicon thin film of not less than 40% of a deposition crystallization molar fraction may be used. The thickness of the photoelectric conversion layer 27 is set

up within the limits of 0.1-5 micrometers.
[0019]Said semiconductor layer 28 is deposited with plasma CVD method. As said semiconductor layer 28, the microcrystal silicon thin film or amorphous silicon thin film in which the conductivity-type determination impurity atom was doped is used. The thickness of the semiconductor layer 28 is set up within the limits of 3-100 nm, and is more preferably set up within the limits of 5-50 nm. Said interlayer 24 needs to satisfy the following conditions 1-3.
1) the -- the [1 and] -- prevent the impurity in one unit from being mixed in the unit of another side between the photoelectric conversion units 23 and 25 of two.
2) Prevent generating of the current which contributes to power generation, and the current which flows into an opposite direction between the semiconductor layers 31 of the 1st-2nd photoelectric conversion unit 23, and the 1st semiconductor layer 28 and conductivity type of the 2nd conductivity type of 25 interfaces.
3) Send the incident light of long wavelength mainly to the 2nd photoelectric conversion unit 25 among the incident light by the side of a substrate. Using vacuum deposition and a sputtering technique for example as said interlayer 24, a SnO_2 film or ITO film 29 is produced, and then ZnO film 30 is produced.
[0020]The photoelectric conversion unit 25 of another side comprises the semiconductor layer 31 of the 1st conductivity type, the photoelectric conversion layer 32, and the semiconductor layer 33 of the 2nd conductivity type.
[0021]Said semiconductor layer 31 is deposited with plasma CVD method, and either the microcrystal silicon thin film in which the conductivity-type impurity atom was doped, or an amorphous silicon thin film is used. In the case of a p type layer, as an impurity atom, boron atoms are used for the semiconductor layer 31, for example. The thickness of the semiconductor layer 31 is set up within the limits of 3-100 nm, and is more preferably set up within the limits of 5-50 nm.
[0022]Said photoelectric conversion layer 32 is obtained by

forming a microcrystal silicon thin film or an amorphous silicon thin film with plasma CVD method. As said photoelectric conversion layer 32, non-doped i type amorphous silicon thin film and i type microcrystal silicon thin film of not less than 40% of a deposition crystallization molar fraction may be used. The thickness of the photoelectric conversion layer 32 is set up within the limits of 0.1-5 micrometers.

[0023]Said semiconductor layer 33 is deposited with plasma CVD method. As said semiconductor layer 33, the microcrystal silicon thin film or amorphous silicon thin film in which the conductivity-type determination impurity atom was doped is used. The thickness of the semiconductor layer 33 is set up within the limits of 3-100 nm, and is more preferably set up within the limits of 5-50 nm.

[0024]On said photoelectric conversion unit 25, the transparent conductive film 34 which consists of at least one or more layers chosen from ITO, ZnO, etc. is formed. On this transparent conductive film 34, the metal electrode 35 of at least one or more metal chosen from aluminum, Ag, Au, Cu, Pt, etc. or these alloys is formed by a sputtering technique or vacuum deposition. some surface electrodes 22 on said substrate 21 -- upwards, the aluminum electrode 36 as an electrode for current collection is formed.

[0025]

[Example]Hereafter, the tandem-die thin film crystalline substance silicon solar cell concerning the example of this invention is explained.

(Example 1) The tandem-die solar cell of a two-step lamination type as shown in drawing 1 was produced as Example 1. First, the 600-nm-thick SiO_2 film is formed by the heat CVD method as the surface electrode 22 on the glass substrate 21. On said surface electrode 22, the p type amorphous silicon layer 26 with a thickness of 15 nm by which the boron dope was carried out, the amorphous silicon photoelectric conversion layer 27 with a non-doped thickness of 300 nm, and the 30-nm-thick n type amorphous silicon layer 28 by which the phosphorus dope was

carried out, It is formed by plasma CVD method, respectively, and the 1st step of pin photoelectric conversion unit 23 is formed.

[0026]The interlayer 24 is formed on said photoelectric conversion unit 23. Using a sputtering technique, the interlayer 24 produces the SnO_2 film 29 of 50 nm of thickness, and then produces ZnO film 30 of 50 nm of thickness. Here, what doped gallium, indium, yttrium, silicon, or aluminum may be used for ZnO film 30.

[0027]On said interlayer 24, the 2nd step of pin photoelectric conversion unit 25 is formed. The p type semiconductor layer 31 which the photoelectric conversion unit 25 becomes from p type microcrystal silicon, It comprised the photoelectric conversion layer 32 which consists of microcrystal silicon, and the n type semiconductor layer 33 which consists of n type microcrystal silicon, and each class 31-33 is deposited by the same method as the p type semiconductor layer 26 of the 1st step of photoelectric conversion unit 23, the photoelectric conversion layer 27, and the n type semiconductor layer 28.

[0028]On the 2nd step of photoelectric conversion unit 25, an 80-nm-thick transparent conductive ITO film is formed in a sputtering technique as the transparent conductive film 34, and Ag electrode 35 for current extraction is formed by vacuum deposition on it.

[0029](Example 2) The tandem-die solar cell of a two-step lamination type as shown in drawing 1 was produced as Example 2. First, the 600-nm-thick SnO_2 film is formed by the heat CVD method as the surface electrode 22 on the glass substrate 21. On said surface electrode 22, the p type amorphous silicon layer 26 with a thickness of 15 nm by which the boron dope was carried out, the amorphous silicon photoelectric conversion layer 27 with a non-doped thickness of 300 nm, and the 30-nm-thick n type amorphous silicon layer 28 by which the phosphorus dope was carried out, It is formed by plasma CVD method, respectively, and the 1st step of pin photoelectric conversion unit 23 is formed.

[0030]The interlayer 24 is formed on said photoelectric conversion unit 23. Using a sputtering technique, the interlayer 24 produces ITO film 29 of 50 nm of thickness, and then produces ZnO film 30 of 50 nm of thickness. Here, what doped gallium, indium, yttrium, silicon, or aluminum may be used for ZnO film 30.
[0031]On said interlayer 24, the pin photoelectric conversion unit 25 of the 2nd step of 3-micrometer thickness is formed. The p type semiconductor layer 31 which the photoelectric conversion unit 25 becomes from p type microcrystal silicon, It comprised the photoelectric conversion layer 32 which consists of microcrystal silicon, and the n type semiconductor layer 33 which consists of n type microcrystal silicon, and each class 31-33 is deposited by the same method as the p type semiconductor layer 26 of the 1st step of photoelectric conversion unit 25, the photoelectric conversion layer 27, and the n type semiconductor layer 28.
[0032]On the 2nd step of photoelectric conversion unit 25, an 80-nm-thick transparent conductive ITO film is formed in a sputtering technique as the transparent conductive film 34, and Ag electrode 35 for current extraction is formed by vacuum deposition on it.
[0033](Comparative example) Two steps of tandem-die solar cells were produced by the same method as Example 1 except the interlayer who shows drawing 2 not existing as a comparative example.
[0034]Drawing 3 shows the graph of comparison of the short-circuit current of Example 1, Example 2, and a comparative example. The short-circuit current of the tandem-die solar cell of Example 1 and Example 2 was improving substantially compared with 1.3, 1.4, and the case of a comparative example, respectively, and it became clear that it had big photoelectric conversion efficiency.
[0035]
[Effect of the Invention]it explained in full detail above -- as -- this invention -- the -- the [1 and] -- an interlayer

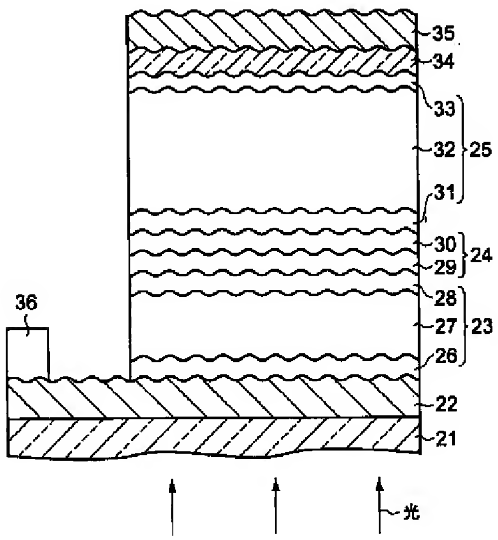
is made to intervene between the photoelectric conversion units of two
Therefore, while being able to prevent a defective part from occurring at the unit community interview rear, the highly efficient tandem-die silicon system thin film photoelectric conversion device which can confine in each unit each wavelength band which has predetermined sensitivity, has it, and has a high photoelectric transfer characteristic, and is excellent also in stability can be provided.
By laminating a crystalline silicon system thin film photoelectric conversion module, It is possible for the reliability and stability of a photoelectric conversion device to be improved remarkably, and to also attain highly efficient-ization of the photoelectric conversion device accompanying improvement in the optical confinement effect, and it can contribute to utilization of a silicon system thin film photoelectric conversion device greatly.

[Brief Description of the Drawings]
[Drawing 1]The typical sectional view of the two-step tandem-die silicon system thin film photoelectric conversion device concerning one embodiment of this invention.
[Drawing 2]The typical sectional view of the two-step tandem-die silicon system thin film photoelectric conversion device concerning the comparative example of this invention.
[Drawing 3]The explanatory view which compared the short-circuit current of the photoelectric conversion device concerning Example 1, Example 2, and a comparative example.
[Drawing 4]The typical sectional view of the conventional tandem-die silicon system thin film photoelectric conversion device.
[Description of Notations]
21 -- Substrate,
22 -- Surface electrode,
23 -- the -- the photoelectric conversion unit of one,

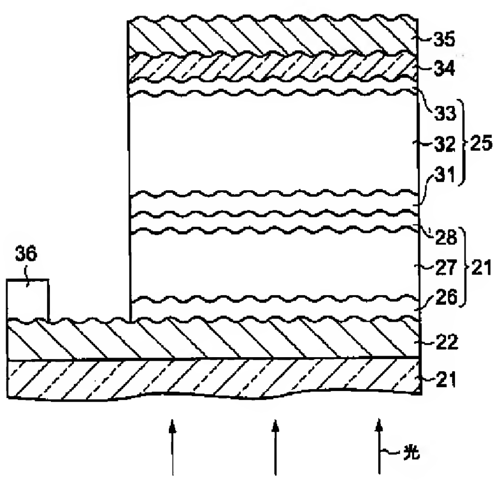
24 -- Interlayer,
25 -- the -- the photoelectric conversion unit of two,
26, 31 -- P type semiconductor layer,
27, 32 -- i type semiconductor layer,
28, 33 -- N type semiconductor layer,
34 -- Transparent conductive film,
35 -- Ag electrode
36 -- Aluminum electrode (electrode for current collection).

DRAWINGS

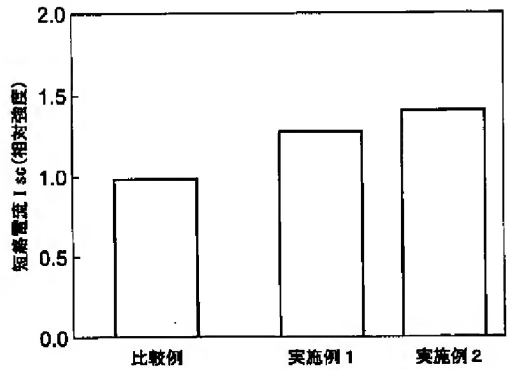
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Drawing 4]